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Rotational Effects on Vibrational Excitation of H_2 on Cu(100)

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Previous experiments have shown that vibrational excitation of H_2 on Cu(111) is accompanied by rotational cooling but were unable to resolve the underlying mechanism. Six-dimensional quantum dynamical calculations on scattering of $(v = 0, j)$ H_2 from Cu(100) strongly suggest that the observed cooling is due to rotational deexcitation occurring simultaneously with vibrational excitation. An alternative mechanism, in which vibrational excitation decreases with increasing initial angular momentum j but j itself is conserved, is ruled out with certainty. [S0031-9007(99)08471-9]

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The dissociation of H_2 on copper is the classic example of activated dissociation of a molecule on a surface. New ideas on surface scattering are often tested on this system, earning it the accolade of "springboard for the development of ideas concerning surface reaction dynamics" [1]. Numerous experiments [2–8] and calculations [9–15] have been performed on H_2 + Cu. The most advanced molecular beam experiments have investigated vibrationally inelastic scattering [3–5], and rotationally elastic [6] and inelastic [7] scattering within the $v = 1$ vibrational state (v is the vibrational quantum number). Complementary information on the scattering and dissociation mechanisms can now be obtained from quantum dynamics calculations modeling the motion in all molecular degrees of freedom [13–15], using accurate potential energy surfaces (PES's) taken from density functional theory (DFT) [16,17].

In surface scattering, the molecular vibration can have a large effect on reaction, and vibrational excitation and reaction can be closely linked. This is especially true for H_2 + Cu. Experiments have shown that vibrationally exciting the incident molecule promotes dissociation [1,2]. Calculations showed that the effect is due to the reaction barrier being "late" (occurring at a large H-H distance r [18]). Experiments also found vibrational excitation ($v = 0 \rightarrow 1$) of H_2 (D_2) on Cu(111) to be unusually efficient, the estimated probabilities ranging from 20%–40% for collision energies (E_i) approaching 1 eV [3–5]. Vibrational excitation and reaction of $v = 0$ H_2 "turn on" at similar energies, suggesting that experiments on vibrational excitation probe the barrier region of the PES [4]. Calculations showed that efficient vibrational excitation occurs if the system exhibits *both* a late barrier *and* a reaction path with a large curvature in front of the barrier [9]. Because these features are present in the region of the PES where H_2 interacts with the top site, vibrational excitation occurs mostly at top sites [12].

An important experimental result is that vibrational excitation from $v = 0$ to 1 is accompanied by rotational cooling (the molecules excited to $v = 1$ have a relatively higher population in lower j levels than the incident $v = 0$ molecules) [4,5]. The mechanism behind the cooling could not be established. Two mechanisms were proposed [5]. In the first mechanism [Fig. 1(b)], j is approximately conserved but the maximum vibrational excitation probability A decreases with j (by a factor of 3 going from $j = 0$ to 7 [4]). This assumption was used to extract absolute probabilities from the data [3–5]. The mechanism can be explained by an orientational effect that causes vibrational excitation to be efficient only for "helicoptering" molecules with $|m_j| \approx j$ [5] (m_j is the magnetic rotational quantum number; the fraction of molecules which have $|m_j| = j$ decreases with j). In the second mechanism, rotational deexcitation accompanies vibrational excitation, so that generally $j' < j$ [Fig. 1(c), j' is the final j]. No distinction could be made between the mechanisms: It was possible to determine the "gain" [5] into different $(v = 1, j)$ states, but not to

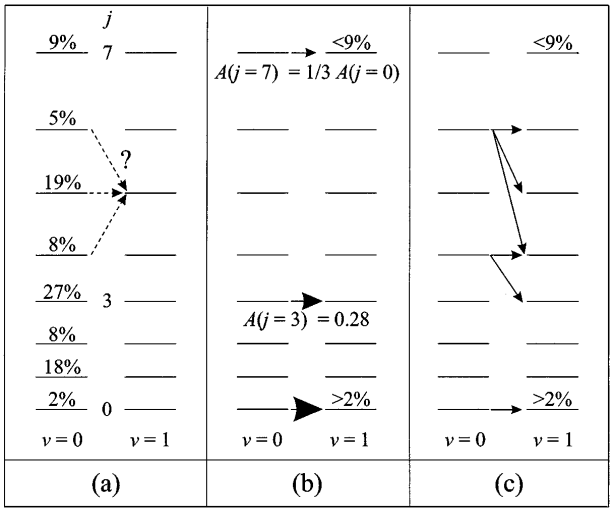

FIG. 1. Illustration of different interpretations of experiments on vibrational excitation. Percentages denote fractional j populations within one vibrational level.

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determine *from which j levels* in $v = 0$ the excitation proceeded [many initial j levels were populated because the rotational temperature ($\approx$2000 K) of the incident H_2 was high [5]—see also Fig. 1(a)].

The observed rotational cooling contains information on specific features of the PES in the important region where vibrational excitation and dissociation compete, but the extraction of this information requires an understanding of the cooling mechanism. The assumption that mainly molecules with $|m_j| = j$ will exhibit vibrational excitation is plausible: because these molecules are mostly parallel to the surface, they can get closer to the barriers in the PES where reaction, but also vibrational excitation, occurs. Calculations [10,11,15] and experiments [8] have shown that helicoptering H_2 ($|m_j| = j$) dissociates better than "cartwheeling" H_2 ($m_j = 0$), and the same could be true for vibrational excitation. On the other hand, the assumption of rotational elasticity on which this mechanism is based is not so plausible in view of the orientational dependence of the PES in the vicinity of the barrier. Also, rotational excitation has been seen in vibrationally elastic scattering of H_2 incident in ($v = 1, j = 0, 1$) on Cu(111) [7]. Individual transitions in which rotational *excitation* accompanied vibrational *deexcitation* were seen in experiments on H_2 + Pd(111) [19], but in this system an important role is played by the surface degrees of freedom [19]. In contrast, the measured vibrational excitation on Cu is independent of surface temperature [3–5].

Theory can decide which mechanism causes the cooling, by computing the state-to-state vibrational excitation probabilities $P(v = 0, j \rightarrow v = 1, j')$ that could not be determined so far by experiments, and by computing the fully initial-state resolved probabilities $P(v = 0, j, m_j \rightarrow v = 1, j')$. We present results of six-dimensional (6D) quantum dynamical calculations on H_2 scattering from Cu(100), for the initial ($v = 0, j = 4$) state whose rotational energy ($\approx$0.14 eV) is closest to the average rotational energy in the beam ($\approx$0.16 eV). Our results strongly suggest that the rotational cooling observed in vibrational excitation of H_2 on Cu(111) is due to a rotationally inelastic mechanism in which the molecule's angular momentum is decreased on average upon vibrational excitation, and rule out that the cooling is due to an orientational effect.

The time-dependent wave packet method [20] was used to compute state-to-state vibrational excitation probabilities $P(v = 0, j, m_j \rightarrow v = 1, j', m_j')$, for scattering at normal incidence. Depending on the level of detail desired, these probabilities are summed over m_j' (or over j' and m_j') and/or degeneracy averaged over m_j. The motion in all six molecular degrees of freedom is described. The main difference with previous 6D applications [13,14] is that the symmetry-adapted treatment used for initial $m_j = 0$ [21] was extended [22,23] to the case $m_j \neq 0$. Details of the dynamics calculations will be provided elsewhere [23]. The dynamics calculations employ a slightly modified version [22] of a 6D PES [17] derived from DFT, using the generalized gradient approximation (GGA), and a slab representation of the metal surface [24]. Details concerning the construction of the PES, such as the GGA used, are in Ref. [17].

Probabilities for rotationally (in)elastic vibrational excitation $P(v = 0, j = 4 \rightarrow v = 1, j')$ are shown in Fig. 2(a). In vibrational excitation from the $j = 4$ state, j is clearly not conserved, $P(v = 0, j = 4 \rightarrow v = 1, j = 2)$ being larger than or comparable to $P(v = 0, j = 4 \rightarrow v = 1, j = 4)$. Transitions in which j is diminished (to $j' < 4$) contribute substantially to the total vibrational excitation probability, especially for lower energies. This suggests that, for $j = 4$, vibrational excitation is accompanied by rotational energy loss, which is one of the explanations that was offered for the observed rotational cooling [5].

The average rotational energy of the molecules that were vibrationally excited in the collision is indeed less than the initial rotational energy for all but the highest E_i investigated [Fig. 3(a)]. Figure 2(a) shows clearly that vibrational excitation is accompanied by strong rotational inelasticity. Nevertheless, by themselves the results of Figs. 2(a) and 3(a) are not enough to establish that the

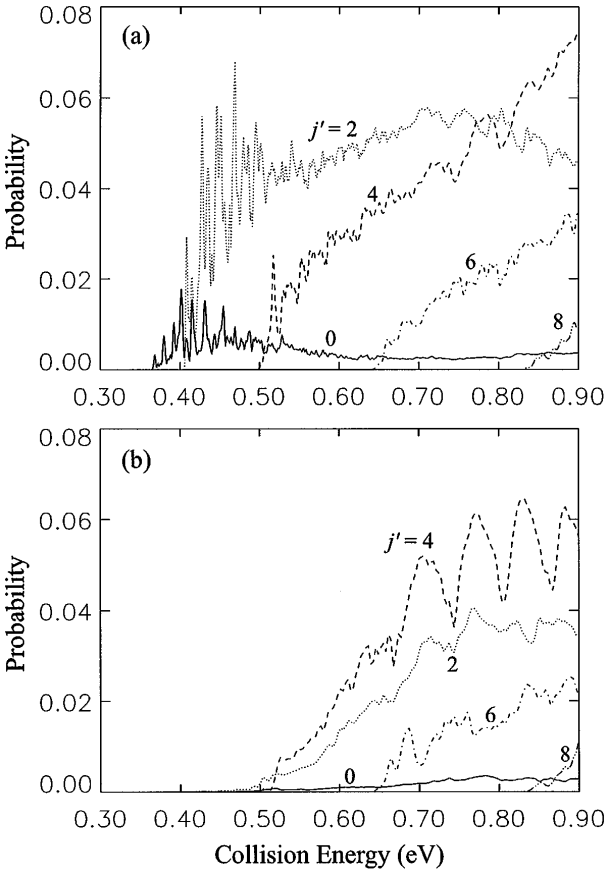

FIG. 2. The probabilities (a) $P(v = 0, j = 4 \rightarrow v = 1, j')$ and (b)$P(v = 0, j = 4, m_j = 4 \rightarrow v = 1, j')$.

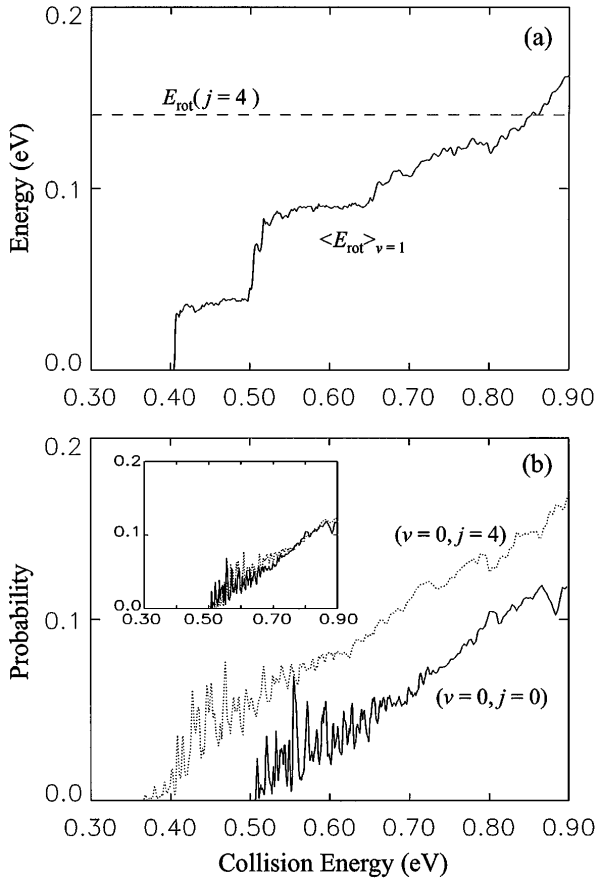

FIG. 3. (a) The average rotational energy of molecules reflected in $v = 1$ is compared to the initial rotational energy. (b) Probabilities $P(v = 0, j = 0 \rightarrow v = 1)$ and $P(v = 0, j = 4 \rightarrow v = 1)$ are shown as a function of E_i and of the total energy (inset).

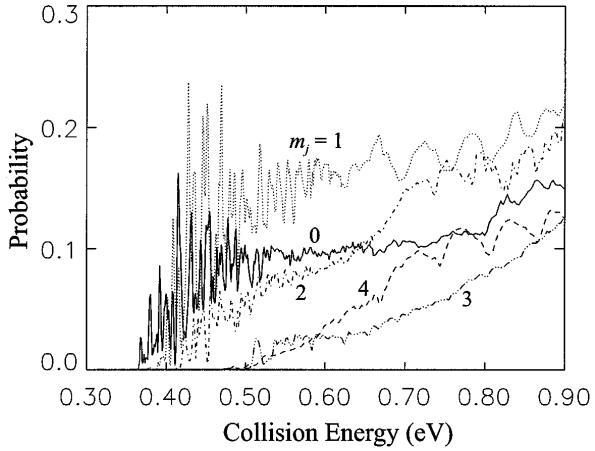

FIG. 4. The probabilities $P(v = 0, j = 4, m_j \rightarrow v = 1)$ are shown.

experimentally observed rotational cooling results from the rotationally inelastic mechanism. For this, we must first rule out the alternative mechanism in which the vibrational excitation probability decreases with the initial value of j.

Figure 3(b) shows that the total vibrational excitation probability $P(v = 0, j \rightarrow v = 1)$ is actually larger for high j ($j = 4$) than for low j ($j = 0$) for the E_i investigated, thereby ruling out the alternative mechanism. Figure 4(a) shows that the idea behind this mechanism was wrong, by presenting total probabilities for vibrational excitation $P(v = 0, j = 4, m_j \rightarrow v = 1)$ which are initial-state selected with respect to m_j. The $P(v = 0, j = 4, m_j \rightarrow v = 1)$ are *smaller* for large $|m_j|$ (3 and 4) than for small $|m_j|$ (0–2).

The finding that $P(v = 0, j \rightarrow v = 1)$ is larger for $j = 4$ than for $j = 0$ at the E_i investigated [Fig. 3(b)] suggests that, at least for $E_i \leq 0.9$ eV, vibrational excitation can also be promoted by putting rotational energy into the incident molecule. When the $P(v = 0, j = 4 \rightarrow v = 1)$ are plotted as a function of the *total* energy, the curves for $j = 0$ and $j = 4$ coincide [inset of Fig. 3(b)]. This suggests that rotational energy can be extremely efficient in promoting vibrational excitation: from our limited set of results (only for $j = 0$ and 4), the efficacy of rotational energy in promoting vibrational excitation is 1.

We now consider which features of the PES relate to the rotational effects on vibrational excitation. We have shown elsewhere that vibrational excitation predominantly occurs in collisions with the top site [12]. At this site, tilting the molecule towards an end-on orientation causes one of the H atoms to point directly towards a surface Cu atom, so that the potential should be especially anisotropic, explaining the observed rotational inelasticity.

Surprisingly, the total vibrational excitation probability is lower for large $|m_j|$ (Fig. 4). This trend is diametrically opposed to the idea that vibrational excitation will only be efficient for $|m_j| = j$. A comparison of the fully initial-state resolved $P(v = 0, j = 4, m_j = 4 \rightarrow v = 1, j')$ [Fig. 2(b)] with the corresponding degeneracy averaged probabilities $P(v = 0, j = 4 \rightarrow v = 1, j')$ [Fig. 2(a)] shows that, especially for low E_i, the lower $P(v = 0, j = 4, m_j \rightarrow v = 1)$ for $m_j = 4$ is due to smaller contributions of transitions to lower j ($j' = 2$ and 0). Transitions to states with $j < m_j$ will be less likely if m_j is approximately conserved in vibrational excitation, and computed $P(v = 0, j = 4, m_j = 4 \rightarrow v = 1, j = 4, m_j')$ presented elsewhere [23] confirm this interpretation. The approximate m_j conservation in vibrational excitation should result from the potential depending only weakly on the angle ϕ (which is conjugate to m_j) at the (top) site where vibrational excitation occurs. *It is this feature of the PES which effectively rules out the rotationally elastic mechanism,* by preventing vibrational excitation from occurring mostly for large m_j. Our calculations may somewhat exaggerate the effect because the PES is taken to be independent of ϕ above the top site [17], but this approximation can be justified on the

ground that dissociation above this site is exothermic for the two limiting values of ϕ (the atoms going to either hollow or bridge sites).

With appropriate caution, our computed *initial-state* selected vibrational excitation probabilities for H_2 + Cu(100) can be compared with the experimental data for H_2 + Cu(111). Experimentally, the extracted *final-state* selected excitation probabilities reach a maximum value at high E_i [for $P(v = 0 \rightarrow v = 1, j = 3)$ this value is 28%] [5]. The largest value we compute for $P(v = 0, j = 4 \rightarrow v = 1)$ [17%, Fig. 3(b)] is lower, but the theory is for a different surface, and the experimental probabilities are too large if vibrational excitation is accompanied by rotational deexcitation [5] as we suggest.

This Letter has presented state-to-state probabilities for vibrational excitation $P(v = 0, j \rightarrow v = 1, j')$. Molecular beam experiments similar to those already performed could, in principle, verify our prediction of strong rotational inelasticity accompanying vibrational excitation. For this, it would be necessary to modify the initial rotational state distribution in the beam in a systematic way, preferentially by transferring the population of one $(v = 0, j)$ level either completely or partly to another $(v = 0, j)$ level prior to the collision. Complete transfer can perhaps be accomplished by extensions of the stimulated Raman adiabatic passage technique to situations where the intermediate level is in the continuum; such extensions are presently being considered [25]. Transfer of a known and sizable fraction of the population can already be achieved by stimulated Raman pumping [19]. By comparing the gains into particular $(v = 1, j')$ states in such experiments with gains measured in experiments performed either without population transfer or with transfer among different levels, it should be possible to extract the desired state-to-state information.

By performing 6D scattering calculations on H_2 + Cu(100), we have established the mechanism behind the experimentally observed rotational cooling accompanying vibrational excitation of H_2 colliding with Cu(111). One of the proposed mechanisms, in which the vibrational excitation probability decreases with the initial angular momentum due to an orientational effect, has been ruled out with certainty. Our calculations strongly support the alternative mechanism, in which the cooling results from vibrational excitation being accompanied by rotational deexcitation. To extract accurate vibrational excitation probabilities, the experiments performed so far should be augmented by quantum scattering calculations performed for many initial states, or they should be extended to allow the extraction of state-to-state information.

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